

# Signature of the existence of the positronium molecule

J. Usukura<sup>1</sup>, K. Varga<sup>2,3</sup>, and Y. Suzuki<sup>4</sup>

<sup>1</sup>*Graduate School of Science and Technology, Niigata University, Niigata 950-2181, Japan*

<sup>2</sup>*Institute of Nuclear Research of the Hungarian Academy of Sciences (ATOMKI), Debrecen,  
H-4001, Hungary*

<sup>3</sup>*Institute for Physical and Chemical Research (RIKEN), Wako, Saitama 351-0198, Japan*

<sup>4</sup>*Department of Physics, Faculty of Science, Niigata University, Niigata 950-2181, Japan*

(February 2, 2008)

## Abstract

The positronium molecule ( $\text{Ps}_2$ ) has not been experimentally observed yet because its tiny (4.5 eV) binding energy cannot be detected when the molecule annihilates by emitting two photons with energy of 0.51 MeV each. It is shown in this paper that the electric dipole transition between the recently found  $L = 1$  excited-state and the  $L = 0$  ground-state with its characteristic photon energy of 4.94 eV is a clear signature of the existence of the positronium molecule and the possibility of its experimental observation is realistic. The probability of this transition is about 17 % of the total decay rate. An other Coulomb four-body system containing positron, HPs (the positronium hydride or hydrogen positride), is also included for comparison.

PACS numbers: 36.10.Dr, 31.15.Pf

## I. INTRODUCTION

Despite the early theoretical prediction of its existence [1], the  $\text{Ps}_2$  molecule has not been experimentally found to date. The difficulty stems from the fact that this system is neutral and therefore it cannot be separated from the positronium atoms (Ps) and its primary decay mode, the annihilation by two-photon emission, is exactly the same as that of the Ps atom. The energy of the photons arising from the annihilation is different in principle: The photons carry 1.02 MeV energy due to the annihilation plus the binding energy of the corresponding system. The binding-energy difference is, however, less than 1 eV and adding it to 1.02 MeV, the energy of the photons coming from the Ps atom or  $\text{Ps}_2$  molecule cannot be experimentally distinguished. The experimental observation of the biexcitons can be considered as an indirect indication of the existence of  $\text{Ps}_2$ .

In our recent Letter [2] we have predicted the existence of a hitherto unknown bound excited-state of the  $\text{Ps}_2$  molecule. In this paper we give a detailed description of this state. We have investigated possible decay modes of this state with a special emphasis on the electric dipole ( $E1$ ) transition to the ground state. It will be shown that the probability of the  $E1$  transition is comparable to that of the annihilation. The unique energy of this transition may possibly be utilized as a sign for the experimental identification of the  $\text{Ps}_2$  molecule.

The stochastic variational method [3,4] has been used to solve the Coulomb four-body problem. In this method the variational trial functions are optimized by gambling: Randomly chosen configurations are probed and most adequate functions are selected to be the basis states.

The Correlated Gaussians (CG) [5] are used as basis functions in this procedure. The CG basis has a long history in atomic and molecular physics and highly accurate calculations are based on this form of basis functions [2,6–10]. The angular part is given by the global vector representation [7]. This approach greatly simplifies the calculations for non-spherical systems by replacing the partial wave expansion with a much simpler representation of the

angular motion.

The hydrogen positride (positronium hydride), HPs, has already been in the focus of intensive theoretical and experimental investigation. This is an ideal system to test the SVM. We compare the properties of the  $\text{Ps}_2$  and HPs molecules.

The plan of this paper is as follows. In sect. II we give a brief description of the trial function and the stochastic variational method. In sect. III the results are presented. The main results of the paper are summarized in sect. IV. In Appendices A-D we collect some basic ingredients which are used in the present study in order to help readers reproduce our results: formulae of the matrix elements in the CG basis, the separation of the center-of-mass motion from the CG basis, the use of Sherman-Morrison formula in selecting nonlinear parameters, and the symmetry requirement for the trial wave function of the  $\text{Ps}_2$  molecule.

## II. THE CALCULATION

A system of two electrons with mass  $m$  and two positive unit charges of mass  $M$  is considered. Their relative mass is characterized by the ratio  $\sigma = m/M$ , and the positronic limit is realized by  $\sigma = 1$ . (Though we consider the case of  $\sigma = 1$  in this paper, the extension to other  $\sigma$  values is straightforward, so we give a formulation assuming an arbitrary mass ratio.) The Hamiltonian of the system reads as

$$H = \sum_{i=1}^4 T_i - T_{\text{cm}} + \sum_{i<j} \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (1)$$

where  $q_i$  and  $\mathbf{r}_i$  are the charges and the position vectors of the particles. Particle labels 1 and 3 denote the positive charges, while labels 2 and 4 denote the negative charges. A relative coordinate system is introduced by defining  $\mathbf{x}_1$  and  $\mathbf{x}_2$  as the distance vectors between the positive and negative charges in the first and second atom, and  $\mathbf{x}_3$  as the distance vector between the center-of-masses of the two atoms:

$$\mathbf{x}_1 = \mathbf{r}_1 - \mathbf{r}_2, \quad (2)$$

$$\mathbf{x}_2 = \mathbf{r}_3 - \mathbf{r}_4, \quad (3)$$

$$\mathbf{x}_3 = \frac{M\mathbf{r}_1 + m\mathbf{r}_2}{M + m} - \frac{M\mathbf{r}_3 + m\mathbf{r}_4}{M + m}, \quad (4)$$

$$\mathbf{x}_4 = \mathbf{R} = \frac{M\mathbf{r}_1 + m\mathbf{r}_2 + M\mathbf{r}_3 + m\mathbf{r}_4}{2M + 2m}. \quad (5)$$

We use the abbreviation  $\mathbf{x} = \{\mathbf{x}_1, \dots, \mathbf{x}_4\}$  and  $\mathbf{r} = \{\mathbf{r}_1, \dots, \mathbf{r}_4\}$ .

### A. The wave function

The CG of the form

$$G_A(\mathbf{r}) = \exp\left\{-\frac{1}{2}\tilde{\mathbf{r}}A\mathbf{r}\right\} = \exp\left\{-\frac{1}{2}\sum_{i,j=1}^4 A_{ij}\mathbf{r}_i \cdot \mathbf{r}_j\right\} \quad (6)$$

is very popular in atomic and molecular physics [4–10]. Here  $\tilde{\mathbf{r}}$  stands for a one-row vector whose  $i$ th element is  $\mathbf{r}_i$ . The merit of this basis is that the matrix elements are analytically available and unlike other trial functions (for example, Hylleraas-type functions) one can relatively easily extend the basis for the case of more than three particles. The well-known defects of this basis are that it does not fulfill the cusp condition and its asymptotics does not follow the exponential falloff. This latter problem, especially for bound states, can be cured by taking linear combinations of adequately chosen CGs.

The CG defined above is spherical and can thus describe systems with only  $L = 0$  orbital angular momentum. The usual way to account for the orbital motion in the case of  $L \neq 0$  is the partial-wave expansion. Because of the complexities arising from the evaluation of matrix elements this expansion gets very tedious for more than three particles. To avoid this difficulty the global vector representation [7] is used. In this approach, one defines a vector  $\mathbf{v}$  as a linear combination of the relative coordinates:

$$\mathbf{v} = \sum_{i=1}^4 u_i \mathbf{r}_i, \quad (7)$$

and the non-spherical part of the wave function is represented by a solid spherical harmonic

$$\mathcal{Y}_{KLM}(\mathbf{v}) = v^{2K+L} Y_{LM}(\hat{\mathbf{v}}). \quad (8)$$

The linear combination coefficients  $u_i$  are considered to be variational parameters and their optimal values are to be determined by the SVM as will be discussed later. The details and examples can be found in [7].

The calculation of the matrix elements for the space part of our basis function

$$f_{KLM}(u, A, \mathbf{r}) = G_A(\mathbf{r})\mathcal{Y}_{KLM}(\mathbf{v}) \quad (9)$$

is given in [7]. In the special case of  $K = 0$  the matrix elements can be written in much simpler form. This is shown in Appendix A. In the  $K \neq 0$  case, the CG is multiplied by a polynomial of the relative coordinates. In some cases this might be very useful, it can improve the short-distance behavior, for example, but this role can also be played by an appropriate superposition of the exponentials. We use  $K = 0$  in this paper.

The translational invariance of the wave function is ensured by requiring that the parameters  $A$  and  $u$  fulfill some special conditions. As is detailed in Appendix B, these conditions ensure that the motion of the center-of-mass is factorized in a product form.

By combining the CG with the angular and spin parts, the full basis function takes the form

$$\Phi_{kLS} = \mathcal{A}\{\chi_{SM_S} f_{KLM}(u_k, A_k, \mathbf{r})\}, \quad (10)$$

with an appropriate spin function  $\chi_{SM_S}$ , where “ $k$ ” is the index of the basis states and  $\mathcal{A}$  is an antisymmetrizer for the identical fermions. In the positronium limit ( $\sigma = 1$ ) the Hamiltonian becomes invariant with respect to the interchange of positive and negative charges. Therefore the basis function should have a definite parity under the charge-permutation operator. See Appendix D for the details of the symmetry requirement on the wave function. For the special case with  $S = 0$  and  $M_S = 0$  in which two spins of positive charges and two electron spins are coupled to zero, respectively, the spin part of the wave function reads as

$$\chi_{00} = \frac{1}{2}(|\uparrow\uparrow\downarrow\downarrow\rangle - |\uparrow\downarrow\downarrow\uparrow\rangle - |\downarrow\uparrow\uparrow\downarrow\rangle + |\downarrow\downarrow\uparrow\uparrow\rangle). \quad (11)$$

(Note that particles 1 and 3 are positive unit charges and particles 2 and 4 are electrons.)

Instead of optimizing the parameters of  $A$  it is more advantageous to rewrite Eq. (6) as

$$\exp\left\{-\frac{1}{2}\sum_{i<j}\alpha_{ij}(\mathbf{r}_i-\mathbf{r}_j)^2-\frac{1}{2}\sum_i\beta_ir_i^2\right\}. \quad (12)$$

The relationship between  $\alpha_{ij}, \beta_i$  and  $A$  is

$$\alpha_{ij} = -A_{ij} \quad (i \neq j), \quad \beta_i = \sum_k A_{ki}, \quad (13)$$

where  $\alpha_{ji}$  ( $i < j$ ) is assumed to be equal to  $\alpha_{ij}$ . There are two reasons to choose this form. The first is that in choosing  $\alpha_{ij}$  in this way we deal with a correlation function between the particles  $i$  and  $j$ , while  $A_{ij}$  has no such direct meaning and during the optimization it is more difficult to limit the numerical interval of  $A_{ij}$  to be chosen from. Secondly, one can utilize this specific form to make the individual steps of the parameter selection very fast. By taking a look at the expressions of the matrix elements in Appendix A, it is clear that the main computational load is the calculation of the inverse and determinant of the matrix of the nonlinear parameters. The form in Eq. (44) offers the possibility of the usage of the Sherman-Morrison formula to calculate these quantities, leading to a much faster function evaluation. The details of this step are given in Appendix C.

## B. Electric dipole transition rate

In the positronium limit ( $\sigma = 1$ ) we deal with antiparticles and the electron-positron pair can annihilate. The lifetime of the first excited-state with  $L = 1$  and negative parity is determined by both processes of annihilation and electric dipole transition to the ground state. The width  $\Gamma_{\text{dipole}}$  for the latter process is calculated through the reduced transition probability  $B(E1)$  for the electric dipole operator  $D_\mu = \sum_{k=1}^4 q_k |\mathbf{r}_k - \mathbf{R}| Y_{1\mu}(\widehat{\mathbf{r}_k - \mathbf{R}})$  ( $\mu = -1, 0, 1$ )

$$\Gamma_{\text{dipole}} = \frac{16\pi}{9} \left(\frac{E}{\hbar c}\right)^3 B(E1; 1^- \rightarrow 0^+), \quad (14)$$

with

$$B(E1; 1^- \rightarrow 0^+) = \sum_{\mu} |\langle 00 | D_{\mu} | 1M \rangle|^2, \quad (15)$$

where  $E$  is the excitation energy of the first excited state.

### C. Annihilation rate

The most dominant annihilation of the first excited-state of  $\text{Ps}_2$  is accompanied by the emission of two photons with energy of about 0.5 MeV each. The decay width  $\Gamma_{2\gamma}$  for the annihilation can be estimated through the decay width  $\Gamma_{2\gamma}^{\text{Ps}}$  of the para-positronium in spin-singlet state. This decay width has to be multiplied by the number  $N_0$  of positron-electron pairs which are in spin-singlet state in the  $\text{Ps}_2$ . In the  $\text{Ps}_2$  excited state we have four positron-electron pairs, among which the probability that the pair is in spin-singlet state is 1/4 because the total spin of the first excited-state of  $\text{Ps}_2$  is zero, as will be shown later. ( $N_0 = 4 \times (1/4) = 1$ .) Therefore, to have an estimate for the decay due to the annihilation we can use the formula (2) of [10]:

$$\Gamma_{2\gamma} = N_0 \Gamma_{2\gamma}^{\text{Ps}} \quad (16)$$

with

$$\Gamma_{2\gamma}^{\text{Ps}} = 4\pi \left( \frac{e^2}{mc^2} \right)^2 \hbar c \langle \Psi | \delta(\mathbf{r}_1 - \mathbf{r}_2) | \Psi \rangle = 4\pi \left( \frac{e^2}{\hbar c} \right)^4 \hbar c a_0^{-1} \langle \delta(r_{12}) \rangle, \quad (17)$$

where the probability of finding an electron at the position of a positron,  $\langle \delta(r_{12}) \rangle$ , is the expectation value of  $\delta(\mathbf{x}_1)$  given in a.u., that is  $\langle \delta(r_{12}) \rangle$  is equal to  $a_0^3 \langle \Psi | \delta(\mathbf{r}_1 - \mathbf{r}_2) | \Psi \rangle$  with the Bohr radius  $a_0$ . Roughly speaking, the lifetime is inversely proportional to the probability of finding an electron and a positron at the same position.

### D. The stochastic variational method

To obtain very precise energy, one has to optimize the variational parameters  $u_{ki}$  and  $A_{kij}$  of the trial function. The dimension of basis sets is typically between 100 and 1000,

and each basis state has nine nonlinear parameters. (See Appendix B.) The optimization of a function with a few thousands nonlinear parameters cannot be done efficiently by using a deterministic optimization method, since this could entail the complete reconstruction of the Hamiltonian matrix and diagonalization every time when some of the nonlinear parameters are altered. Moreover, the deterministic search for the optimal value of such a large number of parameters is likely to get trapped in a local minimum.

A procedure based on the stochastic search for the best set of nonlinear parameters can be programmed efficiently [4,11] and is capable of achieving highly accurate results for most few-body systems [2,4,7,12]. The essence of the strategy can be summarized as follows: Let  $\{u_i, A_i\}$  be the nonlinear parameters of the  $i$ th basis function out of the set of  $K$  such basis functions. Then the procedure is

- (1) A succession of different sets of  $(\{u_i^1, A_i^1\}, \dots, \{u_i^{n_s}, A_i^{n_s}\})$  are generated randomly.
- (2) By solving the eigenvalue problem, the corresponding energies  $(E_i^1, \dots, E_i^{n_s})$  are determined.
- (3) The parameter set  $\{u_i^m, A_i^m\}$  which produces the lowest energy is then used to replace the existing  $\{u_i, A_i\}$  set.
- (4) The procedure cycles through the different parameter sets  $(\{u_i, A_i\}, i = 1, \dots, K)$ , successively choosing different sets to minimize the energy until convergence is reached.

The essential reason motivating this strategy is the need to sample different sets of nonlinear parameters as fast as possible. The main advantage is that it is not necessary to recompute the complete Hamiltonian nor it is necessary to solve the generalized eigenvalue problem from scratch each time a new parameter set is generated. By changing the elements of parameter set for each basis function individually, it is necessary to recompute only one row (column) of the Hamiltonian and overlap matrices each time the parameter set  $\{u_i, A_i\}$  is changed. Furthermore, the solution of the generalized eigenvalue problem is also expedited since the Hamiltonian matrix is already diagonal apart from one row and one column.

A similar strategy to the above was used when adding additional terms to the basis.

The speed of the calculation can be further increased if one changes the nonlinear parameters  $A_i$  in a special way. This is described in Appendix C.

The above way of finding the best parameters is certainly very restricted. Even this simple method gives very accurate energies. More sophisticated technique may give better results in a smaller basis size.

### III. RESULTS

The results of calculations for the ground state of HPs and  $\text{Ps}_2$  and the first excited-state of  $\text{Ps}_2$  are reported in this section. The ground states of HPs and  $\text{Ps}_2$  have already been subject to intensive calculations and some of the results obtained before for these systems serve as validation of the SVM. The calculation of the properties of the excited state of the  $\text{Ps}_2$  is the primary focus of this paper. We have previously reported the energy of the ground state of the  $\text{Ps}_2$  and predicted the existence of an excited state of this molecule. This paper reports considerably improved energies by further optimization of the nonlinear parameters of the basis. The further optimization and the increase of the basis dimension has produced an improved wave function and we present different properties of these systems by using that wave function. We show the convergence of the binding energies and various expectation values as a function of the dimension of the basis. The results in the tables are shown for the basis dimensions of  $K = 100, 200, 400, 800, 1200, 1600$ . The basis has been subject of intensive optimizations at these dimensions. Once the optimization at a given basis size has been finished, new basis states have been added (each of them has been selected amongst hundreds of random candidates) to reach the next basis size where the optimization is started again. While the pattern of convergence is a very useful information about the accuracy of the results, one has to keep in mind that this can be distorted by many extraneous factors. This is because one cannot guarantee that the quality of these optimizations is the same. We expect that the stochastic selection of the basis is close to be the optimal choice for lower dimensions, but for large dimensions ( $K = 1200, 1600$ ) the procedure becomes more

time consuming and we have less chance to find the optimal parameters.

### A. Hydrogen Positride, HPs

The boundness of the exotic molecule, HPs, has been known theoretically for many years [13] and it has recently been created and observed in collisions between positrons and methane [14]. The investigation of the stability of positronic atoms has been attracting much attention because positrons can be used as a tool for positron-annihilation spectroscopy in condensed matter physics. The HPs molecule is the simplest but ideal hydride to test the SVM. It is also very intriguing to see the difference between the properties of  $\text{Ps}_2$  and HPs.

The energy calculated by SVM and by other methods are shown in Table I. The proton mass is taken to be infinite. The two electrons are assumed to be in spin-singlet state. The spin states of the proton and the positron can be taken arbitrary. Our result, already at the dimension of  $K = 200$ , is better than the previous calculations. The increase of the basis size improves the energy further. The need of improved accuracy can be clearly seen in Table II, where various expectation values are listed. The expectation value  $\langle r_{e^-e^-}^4 \rangle$ , for example, is much less accurate than the energy and it is considerably improved beyond the dimension  $K = 200$ .

One can compare the expectation values of the separation distances of the particles in the HPs to those in the H and Ps atoms. The average electron-positron distance is  $3.48 a_0$  in HPs, which is slightly different from that in the positronium atom ( $3 a_0$ ). The average electron-proton distance in HPs and H is considerably different ( $2.31 a_0$  and  $1.5 a_0$ ). The average distance between the two positive charges ( $3.66 a_0$ ) is much larger than that in the  $\text{H}_2$  molecule ( $1.41 a_0$ ).

The correlation function defined by

$$C(\mathbf{r}) = \langle \Psi | \delta(\mathbf{r}_i - \mathbf{r}_j - \mathbf{r}) | \Psi \rangle \quad (18)$$

gives more detailed information on a system than just various average distances. This quantity can be calculated by using Eqs. (34) and (35). For the spherical wave function

with  $L = 0$ ,  $C(\mathbf{r})$  is a function of  $r$ , that is, the monopole density, and for the  $L = 1$  wave function, it consists of two terms of monopole and quadrupole densities. Figure 1 displays  $r^2 C(\mathbf{r})$  for various pairs of the constituents of HPs. The two electrons are attracted by the proton, but the proton-electron correlation function is much broader than that in the H atom, while they are separated with its maximum density being at about 2.8 a.u. The positron moves furthest from the proton and has a peak density around at 2.6 a.u. from the electron.

The  $2\gamma$  annihilation rate, calculated from Eq. (16) with  $N_0 = 2 \times (1/4) = 1/2$  and  $\langle \delta_{e^+e^-} \rangle$  of Table II, is found to be  $\Gamma_{2\gamma} = 2.4722 \text{ ns}^{-1}$ , improving the previous estimates [21] by about 0.5%.

### B. Positronium molecule, $\text{Ps}_2$ : Ground state

The energies by SVM are compared to the best previous results in Table III. The result of SVM, again, already at the dimension of  $K = 200$ , is better than the energy of the previous calculations. The increase of the basis size improves the accuracy and the virial factor  $|1 + \langle V \rangle / (2\langle T \rangle)|$  becomes as small as  $0.3 \times 10^{-9}$ , improving the previously best calculation by more than 4 order of magnitude.

The average electron-positron distance is  $4.487 a_0$ , which is about 1.5 times larger than in the positronium atom. The  $2\gamma$  annihilation rate calculated from Eq. (16) by using  $\langle \delta_{e^+e^-} \rangle$  of Table II is found to be  $\Gamma_{2\gamma} = 4.470 \text{ ns}^{-1}$ .

The electron-electron and the electron-positron correlation functions are compared in Fig. 2. The peak position of the electron-electron correlation function is shifted to larger distances compared to the one of the electron-positron correlation function. The electron-positron correlation function in  $\text{Ps}_2$  has much broader distribution than the corresponding function in a Ps atom.

### C. Positronium molecule, $\text{Ps}_2$ : First excited state

In our previous paper we have predicted the existence of the first excited-state of the  $\text{Ps}_2$  molecule. This is a unique bound-state which cannot decay into two Ps atoms due to the Pauli principle. The spin of this state is  $S = 0$  and the orbital angular momentum is  $L = 1$  with negative parity. In this spin state, the  $\text{Ps}_2$  molecule can dissociate into two Ps atoms (bosons) only if the relative orbital angular momentum is even. Consequently, the  $\text{Ps}_2$  molecule with  $L = 1$  and negative parity cannot decay into the ground states of two Ps atoms ( $\text{Ps}(L = 0) + \text{Ps}(L = 0)$ ). The energy of this  $\text{Ps}_2(L = 1)$  state ( $E = -0.334408$  a.u., see Table III) is lower than the energy of the relevant threshold ( $-0.3125$  a.u.), and this state is therefore stable against the autodissociation into  $\text{Ps}(L = 0) + \text{Ps}(L = 1)$ . The binding energy of this state is 0.5961 eV, which is by about 40% more than that of the ground state of  $\text{Ps}_2$  (0.4355 eV).

We have shown in [2] that the bound excited state is essentially a system where two Ps atoms, one in its ground state and the other in its first excited  $P$  state, are weakly coupled. The expectation value of the average electron-positron distance shown in Table V supports this picture: The value of  $7.57 a_0$  in the excited state is 15 % larger than the average ( $6.5 a_0$ ) of the electron-positron distances in the  $L = 0$  ground state of the Ps atom ( $3 a_0$ ) and the  $L = 1$  excited state of the Ps atom ( $10 a_0$ ). We can also estimate the root-mean-square distance  $d = \sqrt{\langle \mathbf{x}_3 \cdot \mathbf{x}_3 \rangle}$  between the two atoms by

$$d^2 = \left\langle \left( \frac{\mathbf{r}_1 + \mathbf{r}_2}{2} - \frac{\mathbf{r}_3 + \mathbf{r}_4}{2} \right)^2 \right\rangle = \frac{1}{4} (2\langle r_{12}^2 \rangle + \langle r_{13}^2 \rangle - 2\langle \mathbf{r}_{12} \cdot \mathbf{r}_{14} \rangle). \quad (19)$$

The symmetry properties of the  $\text{Ps}_2$  wave function are used to obtain the second equality. Using the values of Tables IV and V yields  $d = 6.93$  a.u. for the  $L = 1$  excited state and  $d = 4.82$  a.u. for the  $L = 0$  ground state.

Figure 3 displays the electron-electron and electron-positron correlation functions. As mentioned before, the correlation function for the  $L = 1$  state consists of the monopole and quadrupole densities and their shapes depend on the magnetic quantum number  $M$  of the

wave function. Of course the  $M$ -dependence of the shapes is not independent of each other but is determined by the Clebsch-Gordan coefficient. See Eq. (34). The quadrupole density is contributed only from the  $P$ -wave for the electron-positron relative motion, while the monopole density is contributed by both  $S$ - and  $P$ -waves. Figure 3(a) plots the correlation functions for  $M = 0$  and Fig. 3(b) the correlation functions for  $M = 1$ . As the correlation function is axially symmetric around the  $z$  axis and has a reflection symmetry with respect to the  $xy$  plane, the correlation function sliced on the  $xz$  plane is drawn as a function of  $x$  ( $x \geq 0$ ),  $z$  ( $z \geq 0$ ). The electron-electron correlation function has a peak at the point corresponding to the average distance of 7.57 a.u. The electron-positron correlation function has two peaks reflecting the fact that the basic structure of the second bound-state is a weakly coupled system of a Ps atom in the  $L = 0$  state and another Ps atom in the  $L = 1$  spatially extended state. The peak located at a larger distance from the origin is due to the  $P$ -wave component of the  $\text{Ps}_2$  molecule.

By using the obtained value for  $\langle \delta(r_{12}) \rangle$  in Eq. (16), the lifetime due to the annihilation is estimated to be 0.44 ns. This is about twice of the lifetime of the  $\text{Ps}_2$  ground state. The  $B(E1)$  value is calculated to be  $B(E1) = 0.87e^2a_0^2$ . By combining this value with the dipole transition energy of 4.94 eV, the lifetime due to the electric dipole transition has been found to be 2.1 ns. The branching of the electric dipole transition is thus about 17 % of the total decay rate. Therefore, both branches contribute to the decay of the excited state of the  $\text{Ps}_2$  molecule. Its lifetime is finally estimated to be about 0.37 ns. The excitation energy of 4.94 eV found for the  $\text{Ps}_2$  is different by 0.16 eV from the corresponding excitation energy (5.10 eV) of a Ps atom. This difference seems to be large enough to detect its existence, e.g. in the photon absorption spectrum of the positronium gas.

#### IV. SUMMARY

We have used the Correlated Gaussians combined with the angular functions which are specified by the global vector. Nonlinear parameters of the bases have been determined

by the stochastic variational method. We have considerably improved the results of the previous calculations for the ground state of HPs and  $\text{Ps}_2$ . In addition, we have calculated various expectation values, correlation functions and other properties of the excited state of the  $\text{Ps}_2$  molecule.

The excited state of the  $\text{Ps}_2$  molecule has the orbital angular momentum  $L = 1$ , the spin  $S = 0$ , and negative parity. The excitation energy of the state is 4.941 eV, 0.596 eV below the threshold of  $\text{Ps}(L = 0) + \text{Ps}(L = 1)$ . Though this state is in the continuum of  $\text{Ps}(L = 0) + \text{Ps}(L = 0)$  channel, it is stable against autodissociation into that channel because of the Pauli principle. The main decay mode of this state is the annihilation emitting two photons of about 0.5 MeV each which, except for the tiny binding-energy difference, is equal to the photon energies of Ps atoms. The annihilation decay mode is not useful to confirm experimentally the existence of the  $\text{Ps}_2$  molecule. We have discussed a unique decay mode of the excited state, the electric dipole transition to the ground state. The lifetime due to the electric dipole transition has been calculated to be 2.1 ns, while the lifetime due to the annihilation is 0.44 ns. The electric dipole transition can be used as a signal for experimental confirmation of the  $\text{Ps}_2$  molecule.

This work was supported by OTKA grant No. T17298 (Hungary) and Grant-in-Aid for International Scientific Research (Joint Research) (No. 08044065) of the Ministry of Education, Science and Culture (Japan). The authors are grateful for the use of RIKEN's computer facility which made possible most of the calculations.

## APPENDIX A: EVALUATION OF MATRIX ELEMENTS

In this appendix the matrix elements of the spatial part of the basis functions are given. The method of calculation of these analytical expressions is detailed in Refs. [7,22]. The main aim of this section is to convince the reader that the formulae are particularly simple for the case of  $K = 0$ . The extension to a general  $N$ -body system is straightforward so that we assume that the system contains  $N$  particles.

The basic idea of the calculation of the matrix elements is the usage of the generating function  $g$ :

$$g(\mathbf{s}; A, \mathbf{r}) = \exp\left(-\frac{1}{2}\tilde{\mathbf{r}}A\mathbf{r} + \tilde{\mathbf{s}}\mathbf{r}\right). \quad (20)$$

In the special case of  $K = 0$ , Eq. (9) is obtained from  $g$  by

$$\begin{aligned} f_{0LM}(u, A, \mathbf{r}) &\equiv e^{-\frac{1}{2}\tilde{\mathbf{r}}A\mathbf{r}} \mathcal{Y}_{0LM}(\mathbf{v}) \\ &= \frac{B_L}{L!} \int Y_{LM}(\hat{\mathbf{e}}) \left( \frac{d^L}{d\lambda^L} g(\lambda \mathbf{e} u; A, \mathbf{r}) \right)_{\lambda=0, e=1} d\hat{\mathbf{e}}, \end{aligned} \quad (21)$$

with

$$B_L = \frac{(2L+1)!!}{4\pi}. \quad (22)$$

To abbreviate the expression for the matrix elements we introduce the following notation

$$\langle f' | \mathcal{O} | f \rangle = \langle f_{0LM}(u', A', \mathbf{r}) | \mathcal{O} | f_{0LM}(u, A, \mathbf{r}) \rangle, \quad (23)$$

where  $\mathcal{O}$  stands for the unity, kinetic or potential energy operators. The operators considered here are rotational invariant and thus the matrix elements are diagonal in  $LM$ . Note the prime on  $f$  which is a reminder that the parameters in the ket and the bra may be different.

The use of Eq. (21) in Eq. (23) leads to an expression that the matrix element is derived from that between the generating functions, which becomes a function of parameters  $\lambda, \mathbf{e}, \lambda'$  and  $\mathbf{e}'$ . Here the matrix element between the generating functions can be obtained easily by using the expression

$$\int e^{-\frac{1}{2}\tilde{\mathbf{r}}A\mathbf{r} + \tilde{\mathbf{s}}\mathbf{r}} d\mathbf{r} = \left( \frac{(2\pi)^N}{\det A} \right)^{\frac{3}{2}} e^{\frac{1}{2}\tilde{\mathbf{s}}A^{-1}\mathbf{s}} \quad (24)$$

and its extended formulae. After a power series expansion of the matrix element between the generating functions in terms of  $\lambda, \mathbf{e}, \lambda'$  and  $\mathbf{e}'$ , the derivative and the integration prescribed in Eq. (21) can be carried out straightforwardly [7,22].

The overlap of the trial functions is given by

$$\langle f' | f \rangle = \left( \frac{(2\pi)^N}{\det B} \right)^{\frac{3}{2}} B_L \rho^L. \quad (25)$$

The kinetic energy is expressed by

$$\langle f'|T - T_{\text{cm}}|f\rangle = \frac{\hbar^2}{2} \left( R + LQ\rho^{-1} \right) \langle f'|f\rangle. \quad (26)$$

The matrix elements of a central potential reads as

$$\langle f'|V(|\mathbf{r}_i - \mathbf{r}_j|)|f\rangle = \langle f'|f\rangle \sum_{n=0}^L I(c, n) \frac{L!}{(L-n)!} \left( \frac{\gamma\gamma'}{c\rho} \right)^n, \quad (27)$$

where the integral over the radial form of the potential is expressed with use of Hermite polynomials

$$I(c, n) = \frac{1}{\sqrt{\pi}(2n+1)!} \int_0^\infty V\left(\sqrt{\frac{2}{c}}x\right) e^{-x^2} H_1(x) H_{2n+1}(x) dx. \quad (28)$$

The definitions of the constants in the above expressions are

$$B = A + A', \quad \rho = \tilde{u}' B^{-1} u, \quad \bar{\rho} = \rho - \frac{1}{c} \gamma \gamma'.$$

$$R = 3\text{Tr}(B^{-1} A' \Lambda A), \quad Q = 2 \tilde{u}' B^{-1} A \Lambda A' B^{-1} u.$$

$$c^{-1} = \widetilde{w^{(ij)}} B^{-1} w^{(ij)}, \quad \gamma = c \widetilde{w^{(ij)}} B^{-1} u, \quad \gamma' = c \widetilde{w^{(ij)}} B^{-1} u', \quad (29)$$

where the  $N \times N$  symmetric matrix  $\Lambda$  is defined by  $T - T_{\text{cm}} = (1/2) \sum_{i,j} \Lambda_{ij} \mathbf{p}_i \cdot \mathbf{p}_j$  and  $w^{(ij)}$  is an  $N \times 1$  one-column matrix defined by

$$w_k^{(ij)} = \delta_{ki} - \delta_{kj} \quad (k = 1, \dots, N). \quad (30)$$

The integral in Eq. (28) can be analytically evaluated for several potentials, including Coulomb, exponential or Gaussian potentials. The numerical evaluation for a general potential is a simple matter and one tabulates  $I(c, n)$  for the necessary values of  $c$ . For power law potentials  $V(r) = r^k$ , for example, including the Coulomb interaction, the  $c$ -dependence of the integral  $I(c, n)$  is factored out:

$$I(c, n) = \left( \frac{2}{c} \right)^{k/2} I_n(k), \quad (31)$$

where the remaining integral can be carried out and expressible in terms of the Gamma function:

$$I_n(k) = \frac{1}{\sqrt{\pi}} \sum_{m=0}^n \frac{(-1)^m 2^{2n-2m+1}}{m!(2n-2m+1)!} \Gamma\left(n-m+\frac{k+3}{2}\right). \quad (32)$$

In particular, for the Coulomb force ( $k = -1$ ) we get

$$I_n(-1) = \sqrt{\frac{4}{\pi}} \frac{(-1)^n}{(2n+1)n!}. \quad (33)$$

The correlation function is calculated through the equation

$$\begin{aligned} \langle f' | \delta(\mathbf{r}_i - \mathbf{r}_j - \mathbf{r}) | f \rangle &= \langle f' | f \rangle c^{\frac{3}{2}} e^{-\frac{1}{2}cr^2} \left(\frac{\bar{\rho}}{\rho}\right)^L \sum_{n=0}^L r^{2n} \left(\frac{\gamma\gamma'}{\bar{\rho}}\right)^n \\ &\times \sum_{\kappa=0}^n C_{Ln\kappa} \langle LM \ 2\kappa \ 0 | LM \rangle Y_{2\kappa 0}(\hat{\mathbf{r}}), \end{aligned} \quad (34)$$

where

$$C_{Ln\kappa} = \frac{(-1)^\kappa (2\kappa-1)!! \sqrt{(2L-2\kappa)!(2L+2\kappa+1)!}}{\pi (2L-1)!! 2^{L+1/2} (L-n)! \kappa! (n-\kappa)! (2n+2\kappa+1)!!} \sqrt{\frac{4\kappa+1}{2L+1}}. \quad (35)$$

## APPENDIX B: SEPARATION OF CENTER-OF-MASS MOTION

The transformation between the relative and single-particle coordinates, given by Eqs. (2)-(5), can be defined by the matrix:

$$U = \begin{pmatrix} 1 & -1 & 0 & 0 \\ 0 & 0 & 1 & -1 \\ \frac{M}{m+M} & \frac{m}{m+M} & \frac{-M}{m+M} & \frac{-m}{m+M} \\ \frac{M}{2m+2M} & \frac{m}{2m+2M} & \frac{M}{2m+2M} & \frac{m}{2m+2M} \end{pmatrix}, \quad U^{-1} = \begin{pmatrix} \frac{m}{m+M} & 0 & \frac{1}{2} & 1 \\ \frac{-M}{m+M} & 0 & \frac{1}{2} & 1 \\ 0 & \frac{m}{m+M} & -\frac{1}{2} & 1 \\ 0 & \frac{-M}{m+M} & -\frac{1}{2} & 1 \end{pmatrix}. \quad (36)$$

The transformation between the relative and the single-particle coordinates is given by

$$\mathbf{x} = U\mathbf{r}, \quad \mathbf{r} = U^{-1}\mathbf{x}. \quad (37)$$

Here  $\mathbf{r}$  and  $\mathbf{x}$  are column vectors containing  $(\mathbf{r}_1, \dots, \mathbf{r}_4)$  and  $(\mathbf{x}_1, \dots, \mathbf{x}_4)$ . By this transformation one can express the CG of the single-particle coordinates by the relative coordinates:

$$G_A(\mathbf{r}) = \exp\{-\frac{1}{2}\tilde{\mathbf{r}}A\mathbf{r}\} = \exp\{-\frac{1}{2}\tilde{\mathbf{x}}\mathbf{A}\mathbf{x}\} \equiv G_{\mathbf{A}}(\mathbf{x}), \quad \mathbf{A} = \widetilde{U^{-1}}AU^{-1}. \quad (38)$$

The parameters  $\mathbf{A}_{Ni} = \mathbf{A}_{iN}$ , ( $i = 1, \dots, N-1$ ) connect the relative and center-of-mass variables, and give rise to an undesirable center-of-mass dependence of the wave function.

To have a translational invariant basis, we require that

$$\mathbf{A}_{Ni} = 0, \quad \mathbf{A}_{NN} = c,$$

that is,

$$\sum_{j=1}^N \sum_{k=1}^N A_{jk} U_{ki}^{-1} = 0 \quad (i = 1, \dots, N-1), \quad \sum_{j=1}^N \sum_{k=1}^N A_{jk} = c, \quad (39)$$

where  $c$  is an arbitrary, positive constant common for each basis function. The second condition assures the finite norm of the basis function. By this requirement the relative and center-of-mass motion is separated in the exponential part of the basis function.

To remove the center-of-mass contamination from the angular part, let us express the global vectors  $\mathbf{v}$  in terms of relative coordinates:

$$\mathbf{v} = \sum_{i=1}^N u_i \mathbf{r}_i = \sum_{i=1}^N u_i \sum_{k=1}^N U_{ik}^{-1} \mathbf{x}_k. \quad (40)$$

This identity shows that by requiring

$$\sum_{i=1}^N u_i U_{iN}^{-1} = \sum_{i=1}^N u_i = 0, \quad (41)$$

the global vector becomes translationally invariant.

By fulfilling Eqs. (39) and (41) the basis is free from any problems with the center-of-mass motion. These conditions fix  $N+1$  nonlinear parameters among  $N(N+1)/2 + N = N(N+3)/2$  parameters. For  $N=4$  there remain nine free parameters for each basis function.

## APPENDIX C: SHERMAN-MORRISON FORMULA

As it is shown in Appendix A, the calculation of the matrix elements requires the evaluation of the determinant and inverse of the matrix  $B$ . In the SVM process we probe many

random trials with different matrices. Let us assume that we change the matrix  $A$  of non-linear parameters in such a way that we change the parameter  $\alpha_{ij}$  ( $i \neq j$ ) of the relative motion between particles  $i$  and  $j$  to  $\alpha_{ij} + \lambda$  but keep all other matrix elements unchanged. This is certainly a very restricted way, but in this case the computer time required for the evaluation of the matrix elements tremendously decreases. This change of  $\alpha_{ij}$  produces the following changes in the matrix  $A$  (see Eq. (13)):

$$A_{ij} \rightarrow A_{ij} - \lambda, \quad A_{ji} \rightarrow A_{ji} - \lambda, \quad A_{ii} \rightarrow A_{ii} + \lambda, \quad A_{jj} \rightarrow A_{jj} + \lambda. \quad (42)$$

It is easy to see that this change does not violate the conditions of Eq. (39). Thus the wave function with this modification is still translational invariant. The above change in the matrix  $A$  can be simply expressed by using the vector  $w^{(ij)}$  defined in Eq. (30) as follows:

$$A \rightarrow A - \lambda w^{(ij)} \widetilde{w^{(ij)}}, \quad (43)$$

Note that  $w^{(ij)} \widetilde{w^{(ij)}}$  is an  $N \times N$  matrix, whereas  $\widetilde{w^{(ij)}} w^{(ij)}$  is just a number. As  $B$  is equal to  $A + A'$ , the above change leads to the following modification of  $B$ ,

$$B \rightarrow B - \lambda w^{(ij)} \widetilde{w^{(ij)}}. \quad (44)$$

To calculate the inverse and determinant of the above special form, the Sherman-Morrison formula can be used:

$$\left( B - \lambda w^{(ij)} \widetilde{w^{(ij)}} \right)^{-1} = B^{-1} + \frac{\lambda}{1 - \lambda \widetilde{w^{(ij)}} B^{-1} w^{(ij)}} B^{-1} w^{(ij)} \widetilde{w^{(ij)}} B^{-1}, \quad (45)$$

and

$$\det \left( B - \lambda w^{(ij)} \widetilde{w^{(ij)}} \right) = \left( 1 - \lambda \widetilde{w^{(ij)}} B^{-1} w^{(ij)} \right) \det B. \quad (46)$$

The advantage of this formulae is apparent: By knowing  $B^{-1}$  and  $\det B$  one can easily calculate the right-hand sides of the equations, and the  $\lambda$  dependence is given in a very simple form. For example,  $\widetilde{w^{(ij)}} B^{-1} w^{(ij)}$  simply reduces to  $(B^{-1})_{ii} + (B^{-1})_{jj} - 2(B^{-1})_{ij}$ . Likewise,  $B^{-1} w^{(ij)} \widetilde{w^{(ij)}} B^{-1}$  can also be easily evaluated. To change  $\lambda$ , therefore there is no need for the evaluation of inverses and determinants (which would require  $N^3$  operations) but we get the desired results by a simple multiplication and division.

## APPENDIX D: SYMMETRIZATION OF WAVE FUNCTIONS

### Antisymmetrization

The antisymmetrizer  $\mathcal{A}$  is defined as

$$\mathcal{A} = \frac{1}{\sqrt{n_p}} \sum_{i=1}^{n_p} \varepsilon_i \mathcal{P}_i, \quad (47)$$

where the operator  $\mathcal{P}_i$  changes the indices of identical particles according to the permutation  $(p_1^i, \dots, p_N^i)$  of the numbers  $(1, 2, \dots, N)$ , and  $\varepsilon_i$  is the phase of the permutation. The effect of this operator on the set of the position vectors  $(\mathbf{r}_1, \dots, \mathbf{r}_N)$  is

$$\mathcal{P}_i(\mathbf{r}_1, \dots, \mathbf{r}_N) = (\mathbf{r}_{p_1^i}, \dots, \mathbf{r}_{p_N^i}). \quad (48)$$

By representing the permutations by the matrix

$$(C_i)_{kj} = 1 \quad \text{if} \quad j = p_k^i \quad \text{and} \quad (C_i)_{kj} = 0 \quad \text{otherwise}, \quad (49)$$

(for example, the permutation (3 1 2 4) is represented by

$$C = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \quad (50)$$

while for (1 2 3 4)  $C$  is a unit matrix), the effect of the permutation operator on the single-particle coordinates reads as

$$\mathcal{P}_i \mathbf{r} = C_i \mathbf{r}. \quad (51)$$

By using Eqs. (37) and (51) the permutation of the relative coordinates is expressible as

$$\mathcal{P}_i \mathbf{x} = P_i \mathbf{x} \quad \text{with} \quad P_i = U C_i U^{-1}. \quad (52)$$

The CGs, after permutation, take the form:

$$\mathcal{P}_i G_A(\mathbf{r}) = G_{\tilde{C}_i A C_i}(\mathbf{r}) = G_{\tilde{P}_i \mathbf{A} P_i}(\mathbf{x}) = G_{\widetilde{C_i U^{-1} A C_i U^{-1}}}(\mathbf{x}). \quad (53)$$

In the spin space the permutation operator interchanges the indices of the single-particle spin functions and can be easily evaluated. As a result, the matrix element of any spin-independent operator  $\mathcal{O}$  which is symmetrical with respect to the permutation of identical particle coordinates can be written in the following form:

$$\begin{aligned} & \langle \mathcal{A} \{ \chi_{SM_S} f_{KLM}(u', A', \mathbf{r}) \} | \mathcal{O} | \mathcal{A} \{ \chi_{SM_S} f_{KLM}(u, A, \mathbf{r}) \} \rangle \\ &= \sum_{i=1}^{n_p} c_i \langle f_{KLM}(u', A', \mathbf{r}) | \mathcal{O} | f_{KLM}(\tilde{C}_i u, \tilde{C}_i A C_i, \mathbf{r}) \rangle, \end{aligned} \quad (54)$$

where the coefficients  $c_i$  have the form

$$c_i = \varepsilon_i \langle \chi_{SM_S} | \mathcal{P}_i | \chi_{SM_S} \rangle. \quad (55)$$

Since the antisymmetrizer is a projector onto an antisymmetric state, only ket (or bra) function needs to be antisymmetrized.

The particular value of the coefficient  $c_i$  depends only on the spin function of the system. In the case of  $\text{Ps}_2$  two positrons must be antisymmetrized and likewise two electrons must be in antisymmetric states. Therefore, the antisymmetrizer for this system is given by  $\mathcal{A} = (1 - P_{13})(1 - P_{24})$ , where  $P_{ij}$  is the transposition of particle labels  $i$  and  $j$ . Thus  $\mathcal{A}$  has four permutations ( $n_p = 4$ ) and we can identify

$$\mathcal{P}_1 = 1, \quad \mathcal{P}_2 = P_{13}, \quad \mathcal{P}_3 = P_{24}, \quad \mathcal{P}_4 = P_{13}P_{24}. \quad (56)$$

The corresponding phases are  $\varepsilon_1 = 1, \varepsilon_2 = -1, \varepsilon_3 = -1, \varepsilon_4 = 1$  and the matrices  $C$  are given as follows:

$$C_1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \quad C_2 = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \quad C_3 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}, \quad C_4 = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}. \quad (57)$$

The spin function  $\chi_{00}$  of Eq. (11) is antisymmetric in both of the positron spin coordinates and the electron spin coordinates. Thus the spin matrix element  $\langle \chi_{SM_S} | \mathcal{P}_i | \chi_{SM_S} \rangle$  turns out to be equal to  $\varepsilon_i$  and we have  $c_1 = c_2 = c_3 = c_4 = 1$ .

### Charge symmetry

The Hamiltonian  $H$  for  $\text{Ps}_2$  has charge-exchange symmetry, that is, it is invariant under the exchange of the positive and negative charges: Letting  $P$  denote the charge-permutation operator, we have

$$HP\psi = PH\psi = EP\psi. \quad (58)$$

Therefore, the non-degenerate eigenstate of the Hamiltonian is also the eigenstate of the charge-permutation operator. In the  $\text{Ps}_2$  the ground state is even ( $\pi = +1$ ) under  $P$ , while the  $L = 1$  excited state turns out to be odd ( $\pi = -1$ ).

Consider the case of  $\text{Ps}$  ( $e^+e^-$ ). This system is represented by the coordinate  $(\mathbf{r}_2 - \mathbf{r}_1)$ . The charge permutation is thus equivalent to the parity operation. Since the parity is  $(-1)^L$  for the state with orbital angular momentum  $L$ , the eigenvalue of charge-permutation operator is also  $(-1)^L$ . The signs of  $\mathbf{x}_1$  and  $\mathbf{x}_2$  change with respect to the charge permutation  $P_{12}P_{34}$ , while  $\mathbf{x}_3$  does not. Assume that the  $\text{Ps}_2$  has partial waves  $l_1$ ,  $l_2$  and  $l_3$  corresponding to the motion described with  $\mathbf{x}_1$ ,  $\mathbf{x}_2$  and  $\mathbf{x}_3$ , respectively. When charges are permuted, the wave function  $\psi$  become  $(-1)^{l_1}(-1)^{l_2}\psi$ . Then  $P\psi = \psi$  for the  $S$  state with  $l_1 = l_2 = 0$ , while  $P\psi = -\psi$  for the  $P$  state with  $l_1 = 0$  and  $l_2 = 1$ .

The non-vanishing matrix element of the electric dipole transition supports that the first excited  $P$ -state is odd under the charge permutation. This is because the electric dipole operator  $\mathbf{D}$  has the following form except for the constant:

$$\mathbf{D} = e(\mathbf{r}_1 - \mathbf{R}) - e(\mathbf{r}_2 - \mathbf{R}) + e(\mathbf{r}_3 - \mathbf{R}) - e(\mathbf{r}_4 - \mathbf{R}), \quad (59)$$

which changes sign under the charge permutation. Therefore, if the excited  $P$ -state is even under the charge permutation, then the electric dipole matrix element between the  $P$  state and the ground state would identically vanish.

The charge-permutation operator  $P$  is given by  $P_{12}P_{34}$  or  $P_{14}P_{32}$ . When the wave function  $\psi$  is already antisymmetrized for two positrons and for two electrons, then we can see that both operators give the same effect. To understand this we use the following identity

$$P_{14}P_{32}\psi = (P_{12}P_{34})^2P_{14}P_{32}(P_{13}P_{24})^2\psi = P_{12}P_{34}P_{13}P_{24}\psi = P_{12}P_{34}\psi. \quad (60)$$

Thus the basis function for the  $\text{Ps}_2$  molecule with definite charge-permutation symmetry is given by operating with the following operator  $\mathcal{C}$  on the function:

$$\mathcal{C} = \frac{1}{\sqrt{8}}(1 + \pi P_{12}P_{34})(1 - P_{13})(1 - P_{24}). \quad (61)$$

The evaluation of matrix elements between the states with odd charge symmetry can be done in a similar manner to the previous subsection by extending Eqs. (54) and (55). The antisymmetrizer  $\mathcal{A}$  is now replaced with  $\mathcal{C} = (1/\sqrt{8})\sum_{i=1}^8 \varepsilon_i \mathcal{P}_i$ , where new  $\mathcal{P}_i$  are defined by

$$\mathcal{P}_5 = P_{12}P_{34}, \quad \mathcal{P}_6 = P_{12}P_{34}P_{13}, \quad \mathcal{P}_7 = P_{12}P_{34}P_{24}, \quad \mathcal{P}_8 = P_{12}P_{34}P_{13}P_{24}, \quad (62)$$

and the corresponding phases are  $\varepsilon_5 = -1$ ,  $\varepsilon_6 = 1$ ,  $\varepsilon_7 = 1$ ,  $\varepsilon_8 = -1$ . The matrices  $C_i$  corresponding to  $\mathcal{P}_i$  are given below:

$$C_5 = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \quad C_6 = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \quad C_7 = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \end{pmatrix}, \quad C_8 = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}. \quad (63)$$

It is easy to evaluate the coefficients  $c_i$ . For the spin function  $\chi_{00}$  of Eq. (11), we get  $c_5 = c_6 = c_7 = c_8 = -1$ .

## REFERENCES

- [1] E. A. Hylleraas and A. Ore, Phys. Rev. **71**, 493 (1947).
- [2] K. Varga, J. Usukura, and Y. Suzuki, Phys. Rev. Lett. **80**, 1876 (1998).
- [3] V. I. Kukulin and V. M. Krasnopol'sky, J. Phys. G**3**, 795 (1977).
- [4] K. Varga and Y. Suzuki, Phys. Rev. C**52**, 2885 (1995); Phys. Rev. A **53**, 1907 (1996).
- [5] S. F. Boys, Proc. R. Soc. London Ser. A**258**, 402 (1960); K. Singer, *ibid.* A**258**, 412 (1960).
- [6] D. Kinghorn and L. Adamowicz, J. Chem. Phys. **106**, 4589 (1997).
- [7] Y. Suzuki, J. Usukura and K. Varga, J. Phys. B**31**, 31 (1998).
- [8] P. M. Kozlowski and L. Adamowicz, Phys. Rev. A**48**, 1903 (1993).
- [9] D. B. Kinghorn and R. D. Poshusta, Phys. Rev. A**47**, 3671 (1993).
- [10] A. M. Frolov, S. I. Kryuchkov and V. H. Smith, Jr. , Phys. Rev. A**51**, 4514 (1995).
- [11] K. Varga and Y. Suzuki, Comp. Phys. Commun. **106**, 157 (1997).
- [12] G. Ryzhikh, J. Mitroy and K. Varga, J. Phys. B., in press.
- [13] A. Ore, Phys. Rev. **83**, 665 (1951).
- [14] D. M. Schrader, F. M. Jacobson, N-E. Frandsen and U. Mikkelsen, Phys. Rev. Lett. **69**, 57 (1992).
- [15] D. C. Clary, J. Phys. B**9**, 3115 (1976).
- [16] Y. K. Ho, Phys. Rev. A**34**, 609 (1986).
- [17] T. Yoshida and G. Miyako, Phys. Rev A**54**, 4571 (1996).
- [18] D. Bressanini, M. Mella, and G. Morosi, Phys. Rev. A**57**, 1678 (1998).

- [19] A. M. Frolov and V. H. Smith, Jr., J. Phys. B**29**, L433 (1996); Phys. Rev. A**55**, 2662 (1997).
- [20] D. Bressanini, M. Mella, and G. Morosi, Phys. Rev. A**55**, 200 (1997).
- [21] A. M. Frolov, and V. H. Smith, Jr., Phys. Rev. A**56**, 2417 (1997).
- [22] Y. Suzuki and K. Varga, *Stochastic Variational Approach to Quantum-Mechanical Few-Body Problems*, submitted to Springer-Verlag.

## TABLES

TABLE I. Comparision of the results of different calculations for the ground-state energy of HPs. The energy is given in atomic units.

Method	Reference	Energy
SVM ( $K = 100$ )	Present	$-0.7891013600$
SVM ( $K = 200$ )	Present	$-0.7891810473$
SVM ( $K = 400$ )	Present	$-0.7891924458$
SVM ( $K = 800$ )	Present	$-0.7891958706$
SVM ( $K = 1200$ )	Present	$-0.7891964226$
SVM ( $K = 1600$ )	Present	$-0.7891965536$
Hylleraas configuration interaction	[15]	$-0.7842$
Exponential trial functions	[16]	$-0.7889$
Diffusion Monte Carlo	[17]	$-0.7891 \pm 0.002$
Diffusion Monte Carlo	[18]	$-0.789175 \pm 0.00001$
Correlated Gaussian basis ( $K = 200$ )	[19]	$-0.7891794$

TABLE II. Expectation values of various quantities for HPs. Atomic units are used.  $K$  is the basis dimension.

	$E$	$-\langle V \rangle / (2\langle T \rangle)$		
$K = 100$	-0.7891013600	1.000001		
$K = 200$	-0.7891810473	1.000003		
$K = 400$	-0.7891924458	1.000002		
$K = 800$	-0.7891958706	1.0000007		
$K = 1200$	-0.7891964226	1.0000004		
$K = 1600$	-0.7891965536	1.0000003		
	$\langle r_{e^-e^-}^4 \rangle$	$\langle r_{e^+e^-}^4 \rangle$	$\langle r_{e^-p}^4 \rangle$	$\langle r_{e^+p}^4 \rangle$
$K = 100$	515.42669	525.13203	193.45055	504.56556
$K = 200$	524.98363	531.24425	197.60909	513.48089
$K = 400$	527.33506	532.59188	198.63996	515.59169
$K = 800$	527.88970	532.94707	198.88278	516.06972
$K = 1200$	527.94660	532.98328	198.90610	516.11702
$K = 1600$	527.96159	532.99639	198.91176	516.13646
	$\langle r_{e^-e^-}^3 \rangle$	$\langle r_{e^+e^-}^3 \rangle$	$\langle r_{e^-p}^3 \rangle$	$\langle r_{e^+p}^3 \rangle$
$K = 100$	83.599992	83.792382	34.789685	84.226327
$K = 200$	84.337498	84.249983	35.120402	84.911659
$K = 400$	84.507962	84.347282	35.195647	85.064112
$K = 800$	84.544707	84.369687	35.211858	85.094386
$K = 1200$	84.548681	84.372106	35.213444	85.097517
$K = 1600$	84.549852	84.372949	35.213895	85.098746
	$\langle r_{e^-e^-}^2 \rangle$	$\langle r_{e^+e^-}^2 \rangle$	$\langle r_{e^-p}^2 \rangle$	$\langle r_{e^+p}^2 \rangle$
$K = 100$	15.803193	15.542251	7.7797451	16.188998
$K = 200$	15.860043	15.575673	7.8062352	16.241186
$K = 400$	15.872464	15.582575	7.8117324	16.252128

$K = 800$	15.874993	15.584009	7.8128668	16.254178
$K = 1200$	15.875286	15.584176	7.8129800	16.254399
$K = 1600$	15.875377	15.584230	7.8130152	16.254480
	$\langle r_{e^-e^-} \rangle$	$\langle r_{e^+e^-} \rangle$	$\langle r_{e^-p} \rangle$	$\langle r_{e^+p} \rangle$
$K = 100$	3.5700072	3.4777333	2.3092381	3.6573544
$K = 200$	3.5738023	3.4797561	2.3110943	3.6607696
$K = 400$	3.5745993	3.4801765	2.3114423	3.6614669
$K = 800$	3.5747568	3.4802575	2.3115152	3.6616016
$K = 1200$	3.5747763	3.4802676	2.3115221	3.6616167
$K = 1600$	3.5747825	3.4802707	2.3115245	3.6616220
	$\langle r_{e^-e^-}^{-1} \rangle$	$\langle r_{e^+e^-}^{-1} \rangle$	$\langle r_{e^-p}^{-1} \rangle$	$\langle r_{e^+p}^{-1} \rangle$
$K = 100$	0.37072021	0.41851818	0.72973620	0.34760250
$K = 200$	0.37058889	0.41850815	0.72971467	0.34749891
$K = 400$	0.37056069	0.41849668	0.72970918	0.34746907
$K = 800$	0.37055594	0.41849614	0.72970858	0.34746293
$K = 1200$	0.37055519	0.41849601	0.72970874	0.34746209
$K = 1600$	0.37055494	0.41849596	0.72970869	0.34746180
	$\langle r_{e^-e^-}^{-2} \rangle$	$\langle r_{e^+e^-}^{-2} \rangle$	$\langle r_{e^-p}^{-2} \rangle$	$\langle r_{e^+p}^{-2} \rangle$
$K = 100$	0.21426165	0.34877458	1.2059515	0.17234727
$K = 200$	0.21396622	0.34911573	1.2069510	0.17221620
$K = 400$	0.21392019	0.34912443	1.2070112	0.17217310
$K = 800$	0.21391300	0.34914011	1.2070561	0.17216589
$K = 1200$	0.21391137	0.34914210	1.2070629	0.17216413
$K = 1600$	0.21391064	0.34914275	1.2070632	0.17216372
	$\langle \mathbf{r}_{e_a^-e_b^-} \cdot \mathbf{r}_{e_a^-e_b^+} \rangle$	$\langle \mathbf{r}_{e^+e_a^-} \cdot \mathbf{r}_{e^+e_b^-} \rangle$	$\langle \mathbf{r}_{pe_a^-} \cdot \mathbf{r}_{pe_b^-} \rangle$	$\langle \mathbf{r}_{pe^+} \cdot \mathbf{r}_{pe^-} \rangle$
$K = 100$	7.9015967	7.6406546	-0.12185159	4.2132458
$K = 200$	7.9300217	7.6456510	-0.12378653	4.2358745

$K = 400$	7.9362320	7.6463425	-0.12449962	4.2406428
$K = 800$	7.9374963	7.6465132	-0.12462952	4.2415176
$K = 1200$	7.9376432	7.6465328	-0.12466320	4.2416014
$K = 1600$	7.9376883	7.6465421	-0.12467313	4.2416325
	$-\langle \nabla_{e^-}^2 \rangle$	$-\langle \nabla_{e^+}^2 \rangle$	$\langle \nabla_{e_a^-} \cdot \nabla_{e_b^-} \rangle$	$\langle \nabla_{e^+} \cdot \nabla_{e^-} \rangle$
$K = 100$	0.65224870	0.27367198	-0.043864431	0.11701815
$K = 200$	0.65232846	0.27369666	-0.043999455	0.11707408
$K = 400$	0.65234077	0.27369750	-0.044052593	0.11707637
$K = 800$	0.65234481	0.27369980	-0.044060768	0.11707718
$K = 1200$	0.652345728	0.27370016	-0.044063957	0.11707760
$K = 1600$	0.652345903	0.27370022	-0.044064366	0.11707739
	$\langle \delta_{e^-e^-} \rangle$	$\langle \delta_{e^+e^-} \rangle$	$\langle \delta_{e^-p} \rangle$	$\langle \delta_{e^+p} \rangle$
$K = 100$	0.0047127	0.0236658	0.1717649	0.0017964
$K = 200$	0.0047873	0.0242912	0.1758767	0.0016985
$K = 400$	0.0044178	0.0243887	0.1761969	0.0016542
$K = 800$	0.0043895	0.0244224	0.1768711	0.0016440
$K = 1200$	0.0043889	0.0244583	0.1771854	0.0016386
$K = 1600$	0.0043867	0.0244611	0.1771862	0.00163857

TABLE III. Total energies of the  $\text{Ps}_2$  molecule in atomic units.  $K$  is the basis dimension.

Method	$\text{Ps}_2(L = 0)$	$\text{Ps}_2(L = 1)$
SVM ( $K = 100$ )	$-0.516000069$	$-0.334376975$
SVM ( $K = 200$ )	$-0.516003119$	$-0.334405047$
SVM ( $K = 400$ )	$-0.516003666$	$-0.334407561$
SVM ( $K = 800$ )	$-0.516003778$	$-0.334408177$
SVM ( $K = 1200$ )	$-0.5160037869$	$-0.334408234$
SVM ( $K = 1600$ )	$-0.516003789058$	$-0.3344082658$
Ref. [19] ( $K = 200$ )	$-0.5160024$	
QMC [20]	$-0.51601 \pm 0.00001$	

TABLE IV. Expectation values of various quantities for the ground state of  $\text{Ps}_2$ . Atomic units are used. The positrons are labeled 1 and 3 and the electrons are 2 and 4. Because of the charge-permutation symmetry, e.g.  $\langle r_{12} \rangle = \langle r_{14} \rangle = \langle r_{32} \rangle = \langle r_{34} \rangle$ .  $K$  is the basis dimension.

	$\langle r_{13}^4 \rangle$	$\langle r_{12}^4 \rangle$	$\langle r_{13}^3 \rangle$	$\langle r_{12}^3 \rangle$	$\langle r_{13}^2 \rangle$	$\langle r_{12}^2 \rangle$
$K = 100$	5161.6174	2786.7091	442.51382	252.36242	46.328357	29.088855
$K = 200$	5194.6167	2803.5558	443.64812	252.94378	46.368857	29.109699
$K = 400$	5199.4736	2805.9782	443.77879	253.00898	46.372453	29.111485
$K = 800$	5201.9725	2807.2389	443.85091	253.04531	46.374698	29.112612
$K = 1200$	5201.9467	2807.2264	443.85059	253.04519	46.374696	29.112613
$K = 1600$	5202.0371	2807.2718	443.85244	253.04611	46.374735	29.112633
	$\langle r_{13} \rangle$	$\langle r_{12} \rangle$	$\langle r_{13}^{-1} \rangle$	$\langle r_{12}^{-1} \rangle$	$\langle r_{13}^{-2} \rangle$	$\langle r_{12}^{-2} \rangle$
$K = 100$	6.0316960	4.4863741	0.22080676	0.36840509	0.073455963	0.30308260
$K = 200$	6.0330476	4.4870759	0.22079128	0.36839678	0.073445434	0.30309811
$K = 400$	6.0331385	4.4871188	0.22079076	0.36839718	0.073444789	0.30310268
$K = 800$	6.0332061	4.4871525	0.22079007	0.36839692	0.073444360	0.30310349
$K = 1200$	6.0332062	4.4871526	0.22079008	0.36839693	0.073444319	0.30310354
$K = 1600$	6.0332070	4.4871530	0.22079007	0.36839693	0.073444303	0.30310361
	$\langle \mathbf{r}_{13} \cdot \mathbf{r}_{12} \rangle$	$\langle \mathbf{r}_{12} \cdot \mathbf{r}_{14} \rangle$	$\langle \delta(r_{13}) \rangle$	$\langle \delta(r_{12}) \rangle$	$\langle \nabla_1 \cdot \nabla_2 \rangle$	$\langle \nabla_1 \cdot \nabla_3 \rangle$
$K = 100$	23.164179	5.9246760	0.0006409	0.0219092	0.13077374	-0.00354409
$K = 200$	23.184429	5.9252702	0.0006309	0.0220330	0.13077237	-0.00354402
$K = 400$	23.186227	5.9252581	0.0006284	0.0220860	0.13077326	-0.00354475
$K = 800$	23.186163	5.9252654	0.0006266	0.0221064	0.13077327	-0.00354466
$K = 1200$	23.187348	5.9252652	0.0006267	0.0221075	0.13077325	-0.00354461
$K = 1600$	23.187368	5.9252651	0.0006259	0.0221151	0.1307732538	-0.0035446132
	$\langle \nabla_1^2 \rangle$	$ 1 + \langle V \rangle / (2\langle T \rangle) $				
$K = 100$	-0.25800339	$0.7 \times 10^{-5}$				
$K = 200$	-0.25800073	$0.2 \times 10^{-5}$				

$$K = 400 \quad -0.25800178 \quad 0.1 \times 10^{-6}$$

$$K = 800 \quad -0.25800188 \quad 0.2 \times 10^{-7}$$

$$K = 1200 \quad -0.25800188 \quad 0.4 \times 10^{-8}$$

$$K = 1600 \quad -0.258001894 \quad 0.3 \times 10^{-9}$$


---



---



---



---



---

TABLE V. Expectation values of various quantities for the excited state of  $\text{Ps}_2$ . Atomic units are used. See the caption of Table IV.

	$\langle r_{13}^4 \rangle$	$\langle r_{12}^4 \rangle$	$\langle r_{13}^3 \rangle$	$\langle r_{12}^3 \rangle$	$\langle r_{13}^2 \rangle$	$\langle r_{12}^2 \rangle$
$K = 100$	17822.007	15534.005	1222.7206	1038.7198	95.950622	80.093853
$K = 200$	17925.902	15603.238	1226.3729	1041.0599	96.072859	80.166513
$K = 400$	17937.861	15611.357	1226.7489	1041.3065	96.084420	80.173591
$K = 800$	17939.361	15612.015	1226.7888	1041.3221	96.085316	80.173768
$K = 1200$	17939.589	15612.121	1226.7948	1041.3249	96.085461	80.173821
$K = 1600$	17939.574	15612.112	1226.7955	1041.3251	96.085514	80.173836
	$\langle r_{13} \rangle$	$\langle r_{12} \rangle$	$\langle r_{13}^{-1} \rangle$	$\langle r_{12}^{-1} \rangle$	$\langle r_{13}^{-2} \rangle$	$\langle r_{12}^{-2} \rangle$
$K = 100$	8.8538933	7.5670069	0.14726627	0.24081436	0.032251179	0.16072903
$K = 200$	8.8572758	7.5686805	0.14724521	0.24082305	0.032232174	0.16080331
$K = 400$	8.8575704	7.5688316	0.14724464	0.24082544	0.032230800	0.16081241
$K = 800$	8.8575804	7.5688194	0.14724481	0.24082635	0.032230213	0.16081476
$K = 1200$	8.8575826	7.5688189	0.14724482	0.24082644	0.032230197	0.16081489
$K = 1600$	8.8575844	7.56881891	0.147244820	0.24082648	0.032230158	0.16081514
	$\langle \mathbf{r}_{13} \cdot \mathbf{r}_{12} \rangle$	$\langle \mathbf{r}_{12} \cdot \mathbf{r}_{14} \rangle$	$\langle \delta(r_{13}) \rangle$	$\langle \delta(r_{12}) \rangle$	$\langle \nabla_1 \cdot \nabla_2 \rangle$	$\langle \nabla_1 \cdot \nabla_3 \rangle$
$K = 100$	47.975311	32.118543	0.0001590	0.0108286	0.09163822	-0.01610247
$K = 200$	48.036429	32.130083	0.0001509	0.0111599	0.09165330	-0.01610824
$K = 400$	48.042210	32.131381	0.0001482	0.0111781	0.09165593	-0.01610939
$K = 800$	48.042658	32.131110	0.0001463	0.0112015	0.09165677	-0.01610973
$K = 1200$	48.042730	32.131091	0.00014627	0.0112016	0.09165683	-0.01610972
$K = 1600$	48.042757	32.131079	0.00014591	0.0112091	0.091656853	-0.016109693
	$\langle \nabla_1^2 \rangle$	$ 1 + \langle V \rangle / (2\langle T \rangle) $				
$K = 100$	-0.1671740	$0.4 \times 10^{-4}$				
$K = 200$	-0.1671984	$0.1 \times 10^{-4}$				
$K = 400$	-0.1672025	$0.4 \times 10^{-5}$				

$$K = 800 \quad -0.1672038 \quad 0.8 \times 10^{-6}$$

$$K = 1200 \quad -0.1672039 \quad 0.5 \times 10^{-6}$$

$$K = 1600 \quad -0.16720401 \quad 0.36 \times 10^{-6}$$


---



---



---

# FIGURES

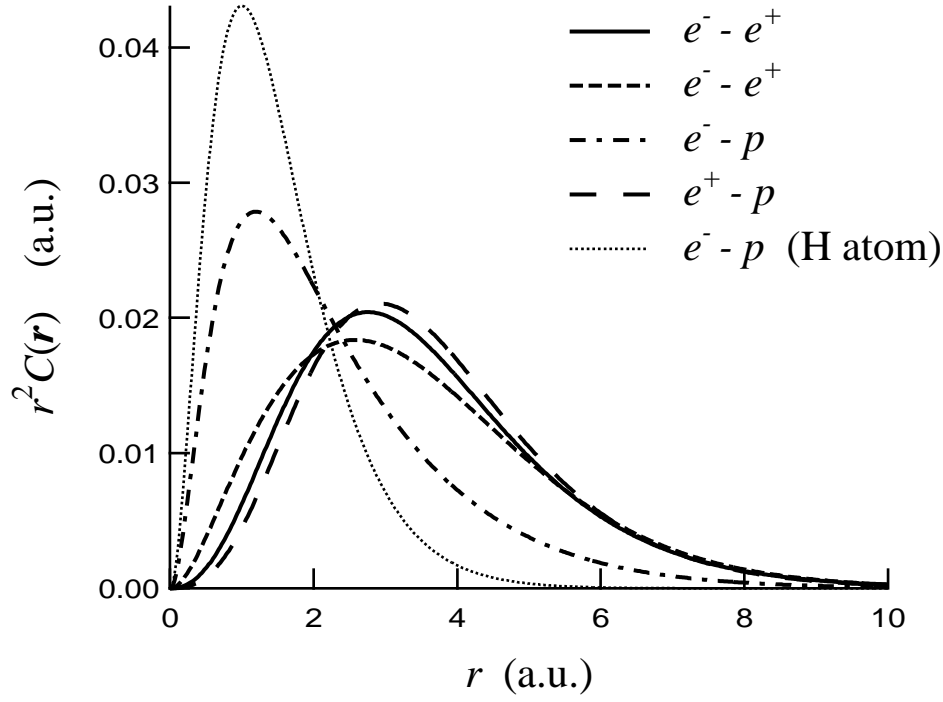


Fig. 1 : The correlation functions  $r^2 C(\mathbf{r})$  for various pairs of the constituents of the hydrogen positride HPs. For the sake of comparison, the electron-proton correlation function of the H atom is also drawn.

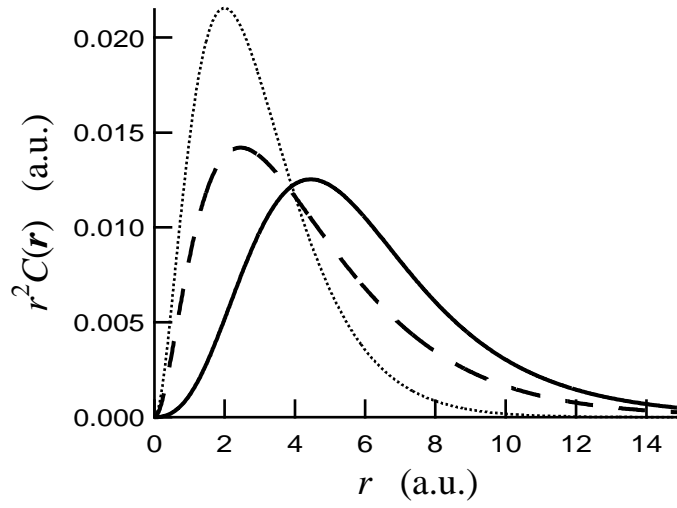


Fig. 2 : The correlation functions  $r^2 C(\mathbf{r})$  for the ground state of the  $\text{Ps}_2$  molecule. The solid curve denotes the electron-electron correlation and the dashed curve the electron-positron correlation. For the sake of comparison, the electron-positron correlation function for the Ps atom is drawn by the dotted curve.

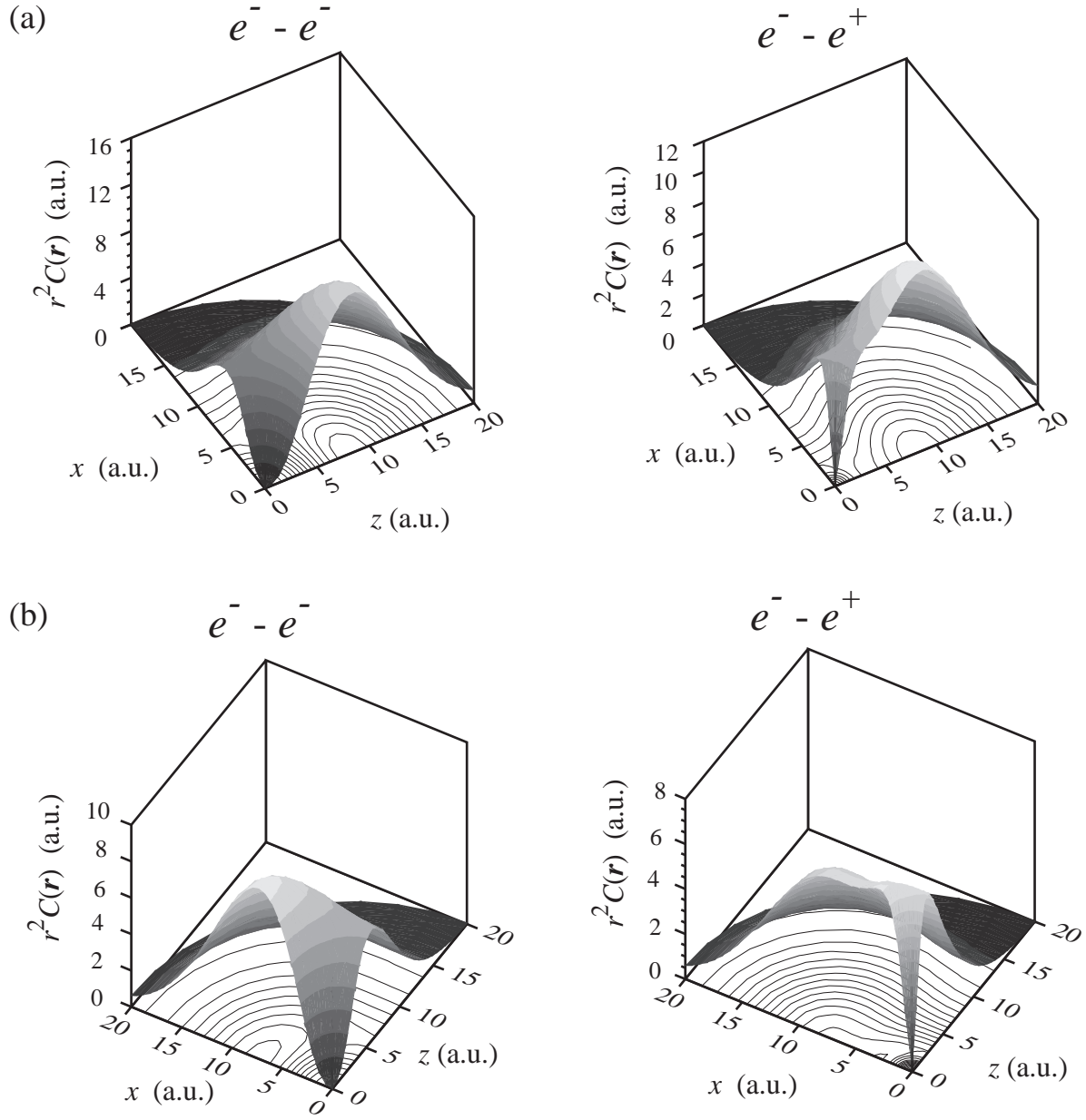


Fig. 3 : The correlation functions  $r^2C(\mathbf{r})$  ( $\mathbf{r} = (x, 0, z)$ ), multiplied by one thousand, for the bound excited-state of the  $\text{Ps}_2$  molecule which has the orbital angular momentum  $L = 1$ , the spin  $S = 0$ , and negative parity. The magnetic quantum number  $M$  is set equal to 0 for (a) and to 1 for (b). Plotted on the  $xz$  plane are the contour maps of the correlation function.